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GENERAL ELECTRIC
3198 Chestnut Street, Philadelphia 4, Penna.

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HUMAN-FACTORS ENGINEERING CONSIDERATIONS IN HANDLING HYPERGOLIC PROPELLANTS

Prepared by H. T. Fisher, Engineering Psychologist and E. M. Coluzzi, Engineering Psychologist

Approved by L. T. Lepine, Manager, Man-Machine Systems

OPERATIONAL SYSTEMS ENGINEERING

REENTRY SYSTEMS SECTION

MISSILE AND SPACE VEHICLE DEPARTMENT

GENERAL ELECTRIC

3198 Chestnut Street, Philadelphia 4, Penna.

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I. INTRODUCTION

A. Scope

Hypergolic liquid propellants in large booster rockets have recently proven their reliability and operational effectiveness as an alternative to the solid rocket when a storable and immediately operable propulsion subsystem is a necessary design criterion. Reentry and flight test vehicles in the past have utilized limited solid rockets for orbital vernier adjustment and orbital velocity change. The feasibility becomes apparent, then, of using liquid hypergolic propellant systems in these vehicles. If such propellants are used, problems will exist when personnel perform the required functions on such a vehicle after its retrieval by air-snatch, as in some present systems, or after direct reentry onto a land or sea mass such as might be proposed in future systems. Since water landings will minimize the toxicity of the propellants, attention will be focused in this report on the problems applicable to land or air-snatch retrieval.

This document discusses these problems and attempts to provide accurate and timely data and information concerning methods, techniques, and equipment in the handling of hypergolic propellants. The information presented could be used to provide data necessary for the generation of Aerospace Ground Equipment (AGE) design criteria for support of an orbiting-type vehicle as discussed above.

Specific information generated herein is as follows:

1. Problems encountered in the handling of hypergolic propellants.

2. Propellant characteristics and associated hazard and health problems.

3. Identification of equipment used in handling hypergolic propellants.

4. Specification of hypergolic propellant handling methods and techniques.

5. Determination of training requirements and equipment.

6. Summary and delineation of follow-on recommendations.

B. Objectives

1. To identify equipment, methods, and techniques required in the handling of hypergolic propellants during retrieval operations.

2. To identify specific vehicle propulsion subsystem characteristics as related to equipment and personnel.

3. To identify those parameters which will insure safety of personnel and equipment.

C. Contents

This document is divided into the following seven sections:

1. Introduction.

2. Problems encountered in handling hypergolic propellants.

3. Propellant characteristics.

4. Equipment used in handling hypergolic propellants.

5. Handling of hypergolic propellants.

6. Hypergolic propellant training.

7. Conclusions and recommendations.

II. PROBLEMS ENCOUNTERED IN HANDLING HYPERGOLIC PROPELLANTS

A. General

1. Normal retrieval operations are complicated by the fact that propellants which are both toxic and hypergolic may be found in or around the vehicle. Many potentially hazardous conditions will be present which must be analyzed in terms of the potential injury to personnel and damage to the vehicle and its payload. This section discusses the problems in these two categories:

a. Hazards to personnel.

b. Damage to flight test vehicle due to handling accidents.

B. Hazards to Personnel

1. Provisions must be made for the detection of, neutralizing of, and protection from the toxic and explosive hazards of the propellant(s).

a. Detection

(1) Liquid: - In the instance of rupture of the lines or the tank, spillage of one or both propellants will occur. If both propellant systems are ruptured, there is great danger that contact between the propellants will cause fire or explosion. The liquid propellant oxidizer and fuel will also cause injury to eyes and mucous membranes and skin burns. Ingestion of liquid will cause internal injury, convulsions, or death. The problem here is to detect with certainty the presence of liquid propellant in the vehicle or in the immediate environment.

(2) Vapor: - Propellant vapor inhaled can be harmful to the mucous membranes, eyes, lungs, liver, kidneys, and other vital organs if present in certain concentrations and/or if inhaled over prolonged periods of time (see Section III). The problem of detection of the maximum allowable concentration by some type of propellant monitoring device or action should be considered very seriously.

b. Neutralizing

(1) The vehicle can be made safe for handling by dousing with water in large amounts. If personnel are exposed to one of the liquid propellants on the skin, the area in question should be washed with water.

(2) Special chemicals, such as triethanolamine, alcohol, and hot nitrogen gas, can be used when a large amount of water is not available and when a small quantity of chemical can be carried. Chemicals can also be used to decontaminate the vehicle more effectively to prevent injury to retrieval

personnel. The availability and expense of these chemicals must be determined for inclusion into this program.

(3) Procedures for the method and extent of neutralizing should be determined. In the propulsion system, the configuration of the tanks might incorporate devices for the quick connection/disconnection of the purging mechanism. Devices located on the propulsion subsystem itself for quick release of tank pressure may or may not be desirable. Procedures for neutralizing the remaining compartments which will undoubtedly have limited accessibility should be determined.

(4) Special precautions must be considered when both propellant systems develop leakage, since the danger of explosion further complicates the hazardous conditions present.

(5) The payload and related hardware, propulsion systems, control and telemetry packages, and the support structure will make the vehicle design extremely crowded. The minimum accessibility necessary to accomplish safe and effective purging and neutralizing should be incorporated into the design configuration.

c. <u>Protection</u>

(1) Certain conditions require the use of suits which provide full protection from external contact and respiration of the toxic propellants. The occurrence of these conditions should be anticipated and provided for. The type of suit which can be used with the hydrazine-type fuel and the nitrogen tetroxide oxidizer should be determined.

(2) In some cases, face shields and/or hoods will give sufficient protection.

(3) Respiratory devices will sometimes be highly desirable for the protection against inhalation of toxic vapors. Self-contained breathing devices can be used within the suit or by themselves. Canister masks may be satisfactory in some cases.

(4) Occasion may arise when personnel who are not completely protected might be exposed to splashing of one (or both) of the propellants. Safety showers can prove to be extremely effectual in the prevention of serious injury or death. The use of a safety shower depends on the determination of its feasibility, type, and portability.

(5) An important method of protection used when operating in a toxic or hazardous environment is the buddy system. The use of this system should be considered and provided during certain portions of the retrieval exercise.

C. Damage to Flight Test Vehicle due to Handling Accidents

1. The handling of the flight test vehicle should be such that the propulsion subsystem does not cause damage to the vehicle. Provisions for lifting and transporting the vehicle and provisions for removal of the payload should facilitate these functions to insure that the payload will be kept in optimum condition.

2. The payload and vehicle might be exposed to the corrosive properties of the propellants or the other chemical used during retrieval.

Recommendations should be made where necessary to prevent damage to the payload. Two parameters to consider might be the duration of exposure and the type and concentration of the chemical (oxidizer, fuel, water, or neutralizing chemicals). The recommendations should consider the type of material used for the payload enclosure, sealing of the payload to the environment, and so on.

3. Protection of the payload from possible explosion or fire should be considered.

D. Summary

This section has outlined the problems encountered in handling hardware with propulsion systems which contain toxic and hypergolic fuels. The problems are delineated according to: (1) hazards of injury to personnel (2) damage to the flight test vehicle due to handling accidents. It is therefore necessary to detect, neutralize, and protect against the hazards of possible injury to personnel. It is also necessary to prevent damage to the payload by safe handling of the potentially corrosive and explosive propellants and by providing protection of the payload from the neutralizing chemicals.

III. PROPELLANT CHARACTERISTICS

A. General

1. Liquid rocket propellants, by requirements for their intended use for high-energy combustion, possess chemical and physical qualities which, without exception, present hazards to operations which demand utmost respect in storage, handling, and use.

2. The greatest possibility for injury to personnel and damage to equipment and hardware is the complacency which may result from day-to-day familiarity or inadequate knowledge of the propellant(s) and conditions of use where combinations of the following factors are involved:

Corrosive properties.	Incompatibility.
Toxicity.	Vaporizing temperatures and rates.
Flammability.	High pressures.
Potential for oxidation.	Large volumes.
Instability.	Extremely low temperatures.
Shock sensitivity.	Remote handling.
Liability to contamination.	

3. While these factors must be carefully considered in the design of equipment, every conceivable hazardous situation in the operation cannot be precluded by design. A need for constant personnel awareness to the factors involved cannot be overemphasized.

4. This section deals with the propellant to be utilized in a program of this nature. This information is not intended as the "final word" for safety during operations nor is it intended to take the place of specific operating procedures/technical instructions but is meant rather as a guide to the designer/system engineer.

5. Individuals whose work involves potential exposure to equipment containing propellants should be thoroughly instructed and trained in the hazards, handling methods and techniques, decontamination measures, and use of emergency procedures of these propellants.

B. Physical Properties

The following paragraphs are intended as a guide to the general and physical description of the propellant ingredients as proposed for a program in which hypergolic propellants are used. Appendixes 1 and 2 provide supplementary data for comparative purposes.

1. Nitrogen Tetroxide

a. General Description

(1) Nitrogen tetroxide (N_2O_4) as a fuel is in equilibrium with nitrogen dioxide (NO_2) and is a clear yellow liquid at atmospheric pressure and temperatures below 70°F. It is used in this form as a strongly oxidizing liquid rocket propellant, being hypergolic with fuels such as UDMH, hydrazine, furfuryl alcohol, and aniline. At atmospheric pressure and temperatures above 70°F, it is a highly toxic gas. Depending upon temperatures, the gas may be colorless (N_2O_4) to dark brown (NO_2).

(2) When moisture content is 0.1% or lower (anhydrous, as received), N_2O_4 will not attack steel. Contact with moisture in the air or with water produces nitrous or nitric acid with its corrosive qualities.

(3) Inhalation of the gas can result in extremely seriously delayed effects on the lower respiratory system. This occurs even with little discomfort at the time of inhalation. Contact of the liquid or gas with normal moisture of the skin or mucous membranes results in formation of nitric acid, which can result in severe burns.

(4) The relatively high boiling point and low vapor pressure of N_2O_4 are important factors in safe handling of the material. Safety precautions required are similar to those for fuming nitric acids, since oxides of nitrogen are the primary noxious constituent of the acids. It should be remembered, however, that larger volumes of this constituent in the pure state are involved.

b. Properties

Formula	N_2O_4.
Molecular weight	92.02.
Freezing point	11.8°F.
Specific gravity (68°F)	1.45.
Boiling point	70.1°F.

Vapor pressure	(86°F)	7.3 psi (gage pressure).
	(100°F)	16.0 psi (gage pressure).
	(120°F)	33.6 psi (gage pressure).
Flammability limits		None. N_2O_4 can form mixtures with combustible materials and is auto-ignitable with propellant fuels.
Solubility		Moderate solubility in water, reacting with it in the presence of oxygen to form nitric acid.
Impact sensitivity		Stable in pure form (see flammability limits, above).
PH base		2-4 (acid condition).

c. Health Hazards and Protection

(1) Fumes from liquid N_2O_4 are very noxious, and breathing them in the higher concentrations for even a brief period of time may result in severe damage to the respiratory system. Fumes evolved from N_2O_4 may have a yellow to dark brown color, the intensity of which is not necessarily an indication of the degree of danger.

The fumes may cause little or no actual discomfort at the time of inhalation and the worker may continue his work feeling quite well although severe lung damage has been suffered, the signs and symptoms of which may not manifest themselves for several hours. These later symptoms may vary considerably, but generally they consist of a burning in the chest accompanied by a sensation of choking and spasmodic coughing. This describes the effects of inhalation in small amounts and recovery with proper medical attention is only a matter of a few hours. In more severe cases, the above symptoms are increased in intensity together with other symptoms, low blood pressure, accompanied by a feeling of faintness, and possible loss of consciousness.

(2) N_2O_4 has a pungent sweetish odor detectable at about 20 ppm. The maximum allowable concentration of N_2O_4 for repeated 8-hour/day exposure is recognized as 5.0 ppm. Delayed pulmonary edema may follow exposure to higher concentrations (100-150 ppm) for a period of only 1/2 to 1 hour, while a few breaths of N_2O_4 at concentrations of 200-700 ppm will produce severe pulmonary damage which may cause death in 5 to 8 hours.

(3) It is imperative that prompt medical treatment be obtained in the event of any exposure or occurrence of the symptoms described. Proper treatment, promptly administered may avert completely the delayed effects of exposure. Should the symptoms occur after working hours, medical personnel should be contacted immediately for instructions. In the event of overexposure, the victim should be carried to a clear atmosphere. He should not be allowed to walk or exert himself. Artificial respiration should be started at once if breathing has ceased.

(4) Contact of N_2O_4 with moisture of the skin or mucous membranes results in the formation of nitric and nitrous acids and corrosive effects. The first symptoms are smarting, itching, and yellow discoloration. If the acid formed is not removed at once, intense pain and severe burns with scarring will result. Lesser exposure may cause chronic skin irritation. Severe and possible permanent damage to the eyes will result from failure to treat burns of the eyes promptly will copious amounts of water. Symptoms of burning and itching demand immediate treatment.

(5) Acid goggles should be worn as minimum protection by anyone entering an N_2O_4 storage or handling area or approaching an unpurged reentry vehicle.

(6) Respiratory protection for the operations listed below, (d) through (g), should consist of a canister mask provided with approved canister for propellants. The mask shall be in place on the operator's face. Protective clothing should consist of a one- or two-piece suit, hood, gloves, and footwear. A self-contained oxygen breathing apparatus in combination with the suit checked for proper operation and a full propellant suit, should be at the retrieval site for operations (a), (b) and (c) below:

(a) During start-up or transfer of propellant.

(b) When opening propellant lines or fittings to the atmospheres.

(c) Purging and cleaning of propellant subsystems.

(d) When working with disconnected lines or equipment that has contained propellant.

(e) When opening any valve, which allows propellant liquid, or vapor to escape in work area.

(f) When tightening connections on a system containing propellants.

(g) When sampling propellant liquids.

(7) The complete protective wearing apparel described above shall also be required for the following operations. Respiratory protection for (a) below shall consist of a Scott Air-Pak (or similar device) in use with mask on face. Item (b) requires a Scott Air-Pak to be worn in readiness for use. Operations (c) and (d) require the wearing of the canister mask in readiness for use.

(a) When fighting a propellant fire. Clean up or repair work to correct a spill or leak.

(b) When acting as a "buddy."

(c) When leak checking under gas pressure if a system has contained propellant but has been drained.

(d) During transfer of propellants after a start-up and checkout of system.

(8) When using vapor detector or otherwise entering areas of known or suspected contamination for investigation, an oxygen breathing apparatus (self-contained) should be used for respiratory protection.

(9) When operators are alerted to storable propellant test or operation upwind, the wearing of a canister mask in readiness for use should be required.

(10) Propellant servicemen and civilian technicians assigned to work on N_2O_4 systems will be given a Chemical Contact Examination for purposes of monitoring current and accumulated propellant exposure. The examination is not a preventive treatment applied to a selected group, but is a matter of providing a written record of current and accumulated propellant dosages.

(11) Any skin or eye contact with N_2O_4 must be followed by immediate flushing of the contaminated area with copious amounts of water.

(a) Contaminated clothing should be removed while under the safety shower.

(b) Eyelids may need to be held open for thorough flushing at eye wash fountains.

(12) Respiratory exposure must be treated by removing the injured to fresh air. Summon help. Apply artificial respiration if breathing has ceased. Summon medical assistance immediately. (Facilities for administering oxygen will be required in the case of acute exposure.)

(13) Prompt medical attention shall be required as a precaution for all exposure regardless of first-aid in the field.

d. Fire Hazards and Protection

(1) N_2O_4 itself is not flammable; however, its action as a strong oxidizer must be considered and provided for in storage and use. N_2O_4 is autoignitable with fuels (see Appendix 1) used as propellants and may under certain conditions promote ignition through heat of nitration with other combustible materials.

(a) Fires involving N_2O_4 burn vigorously and evolve toxic fumes that are injurious to unprotected personnel.

(b) Water is the best extinguishing agent for fires of this type.

(c) N_2O_4 containers exposed to fire should be kept cool by application of water spray.

2. Hydrazine (Anhydrous)

a. General Description

(1) Anhydrous hydrazine N_2H_4 is a clear, colorless, caustic liquid with a characteristic ammoniacal odor. Hydrazine is very hygroscopic, producing white vapors when exposed to air. Its strong potential for reduction, exhibited by ignition when combined with selected oxidizers, is an important factor in its use as a liquid rocket propellant fuel.

(2) Hydrazine is toxic by inhalation and skin contact, requiring specific measures for personnel protection. The recognized MAC is 0.5 ppm. N_2H_4 vapors are flammable.

(3) Hydrazine is not shock-sensitive and is fairly stable when stored in tight containers of compatible construction. A number of materials, however, including iron rust, catalyze the decomposition of N_2H_4 with the release of hydrogen constituting an explosion hazard in a confined space. Hydrazine is subjected to explosion when exposed to oxidizers and when heated in a confined space.

(4) Because of its high reactivity with many common materials, materials for use with N_2H_4 must be carefully selected.

b. Properties

Molecular weight (Anhydrous Hydrazine)	32.05.
Boiling point	236°F.
Freezing point	34.9°F (white crystals---no chemical change in extreme cold; supercools easily. Freezing point can be lowered with monohydrate or to other activities such as ammonia.)
Density of liquid (32°F) (that of water) (122°F)	64.04 lb/cu ft. 61.19 lb/cu ft.
Vapor pressure (32°F)	0.05 psi(absolute).
Flammability limits	Vapor forms explosive mixtures in air at concentrations above 25% by weight.
Autoignition temperature (air s/s)	320°F.
Flash point (open cup)	100°F.
Stability (shock)	Not shock-sensitive.
Stability (heat)	Decomposes at rate below 2% hr at 392°F and 600 psia; explosion temp. 449°F.
Solubility	Very soluble in water. Soluble in higher alcohols and liquid ammonia. Reacts safely with mixtures methyl-alcohol and hydrogen peroxide. Slightly soluble in organic solvents.
Reactivity	Powerful reducing agent reacting with all oxidizers. Hypergolic with fuming nitric acids and nitrogen tetroxide. Corrosive; attacks mild steel, rubber, most common metals, porcelain, and glass.

Compatibility	Satisfactory materials of construction are 303, 304, 410, and 347 s/s, nickel, aluminum (if no free caustic is present), certain polyvinyl resins, and asbestos.
Not compatible with	Copper, zinc, silver, most lubricants and teflon materials (decomposes the latter in the atmosphere).
Decomposition catalysts	Oxides of iron, molybdenum, lead, and mercury, simple copper salts, and most organic materials catalyze the decomposition of N_2H_4 to hydrogen and nitrous oxides.

c. Health Hazards and Protection

(1) Hydrazine readily absorbs moisture from the air forming the monohydrate which is corrosive to the skin and toxic upon inhalation.

(2) Skin splashing results in an intense burning sensation. Exposure to moderate or heavy concentrations of the fumes produces immediate violent irritation of the nose and throat, itching, burning, and swelling of the eyes. Dizziness and nausea may follow within a short time.

(3) Exposure to mild concentrations is not evident at the time of exposure. Symptoms appear several hours later in the form of the same effects described for moderate or heavy concentrations.

(4) Although the vapors are considered toxic, the sharp irritating odor is so intolerable that it becomes almost impossible to breathe quantities to produce permanent damage. In contrast with the vapors, liquid hydrazine can cause permanent damage to the eyes even on short contact.

(5) Acid goggles shall be worn as minimum protection by anyone entering a hydrazine storage or handling area.

(6) Respiratory protection for the operations listed in (d) through (g) below should consist of a canister mask provided with approved canister for propellants such as hydrazine and nitrogen tetroxide. The mask shall be in place on the face. Protective clothing shall consist of a one- or two-piece suit, hood, gloves, and footwear. Self-contained oxygen breathing apparatus and full propellant suits checked for proper operation should be at the retrieval site for operations (a), (b), and (c) below:

(a) During start-up or transfer of propellant.

(b) When opening propellant lines or fittings to atmosphere.

(c) Purging and neutralizing of propellant systems.

(d) When removing disconnected lines or equipment that has contained propellant.

(e) When opening any valve which allows propellant or vapor to escape in work area.

(f) When tightening connections on a system containing propellants.

(g) When sampling liquid.

(7) The complete protective wearing apparel described above shall be required for the following operations. Respiratory protection for (a) below shall consist of a Scott Air-Pak (or similar device) in use with mask on face. Item (b) requires a Scott Air-Pak to be worn in readiness for use. Operations shown as (c) and (d) require the wearing of the canister mask in readiness for use.

(a) When fighting a propellant fire, clean-up or repair work to correct a spill or leak.

(b) When acting as a "buddy."

(c) When checking for leaks under gas pressure if a system has contained propellant but has been drained.

(d) During transfer of propellants after start-up and checkout of system.

(8) While using vapor detector or otherwise entering areas of known or suspected contamination for investigation, a Scott Air-Pak shall be used for respiratory protection.

(9) When operators are alerted to storable propellant test or operation upwind, the wearing of a canister mask in readiness for use should be required.

(10) Propellant servicemen and civilian technicians assigned to work on hydrazine systems will be given a Chemical Contact Examination for purposes of monitoring current and accumulated propellant exposure. The examination is not a preventive treatment applied to a selected group, but is a matter of providing a written record of current and accumulated propellant dosages.

(11) Any skin or eye contact with hydrazine must be followed by immediate flushing of the contaminated area with copious amounts of water.

(a) Contaminated clothing should be removed while under the safety shower.

(b) Eyelids may need to be held open for thorough flushing at eye wash fountains.

(12) Respiratory exposure must be treated by removing the injured to fresh air. Summon help. Apply artificial respiration if breathing has ceased. Summon medical assistance immediately. (Facilities for administering oxygen will be required in the case of acute exposure.)

(13) Prompt medical attention shall be required as a precaution for all exposure regardless of first-aid treatment in the field.

d. Fire Hazards and Protection

(1) Although liquid hydrazine is not flammable, its vapors at 100°F will burn upon introduction of a source of ignition.

(2) Hydrazine in the presence of oxidizing materials (see Appendix 1) presents a serious fire hazard from spontaneous ignition.

(3) Contamination in storage equipment or leaking hydrazine containers will result in decomposition with the evolution of hydrogen which adds to the explosion and fire hazard. Contact of hydrazine with rust on outside surfaces does not present the same hazard, providing leaks or spills are monitored and washed down.

(4) Hydrazine in equipment subjected to exposure to fires will decompose and fire at 320°F.

(a) Hydrazine storage areas should be of noncombustible construction, well-ventilated, and isolated from oxidizing materials and vapors and exposure to fires.

(b) Electrical equipment in hydrazine storage and handling areas should be of the explosion-proof type.

(c) Drums and tanks should be grounded at all times.

(d) "No Smoking" signs should be prominently displayed.

(e) Large volumes of water are recommended as the best extinguishing agent for hydrazine fires. Adequate water supplies should be available at storage locations for fire-fighting and for cooling equipment with water fog.

(5) Products of combustion of hydrazine are toxic.

(a) Fires should be fought from upwind. Fire fighters should use self-contained air breathing equipment.

IV. EQUIPMENT USED IN HANDLING HYPERGOLIC PROPELLANTS

A. General

Due to the nature of the propulsion subsystem design and the field conditions under which this subsystem could be retrieved, there should be maximum consideration for equipment and personnel safety. The assurance of this maximum consideration requires purging and neutralizing equipment, propellant toxicity monitoring devices, and personnel safety equipment.

Continued design review and field evaluation should be instituted in order to insure reliable, simple, and safe operation. The following paragraphs are included to provide equipment design parameters necessary to achieve system requirements.

B. Equipment

1. Purging and Neutralizing Equipment: - A portable device which can purge and neutralize the propulsion subsystem in the vehicle in order to insure the safety of the personnel during retrieval, transportation, storage and removal of the payload from the vehicle. Purging and neutralizing equipment should be considered with the following criteria in mind:

a. The device should be of such a weight and configuration that it can be carried and handled by one person if possible, or by no more than two persons. Provisions should be made for transportation of the purging and neutralizing equipment over any type of terrain. Collapsible and/or portable wheeled carts or containers either separate or integral to the equipment should be considered. It is necessary that the purging and neutralizing equipment be of such design that it may be dropped from the retrieval helicopter(s) and search aircraft along with or as part of the personnel retrieval pack.

b. The purging and neutralizing equipment should also be designed to be self-contained and capable of ejecting the solutions with relatively high volume and pressure.

c. The actual chemicals which may be used for neutralizing the propellants are described in Section V, paragraphs D.1.b. and c.

d. It is anticipated that the purging and neutralizing of the propellant subsystem will be performed adequately upon first contact with the vehicle. It is desirable, because of the extremely dangerous characteristics potentially existing in the use of these propellants, that provisions for making the propellant subsystem safe at any time be maintained in the trucks and in the receiving areas.

e. Positive quick-disconnect hoses and connectors with their corresponding connection points on the propellant tanks and lines should be provided to facilitate ease, rapidity, and reliability of the purging and neutralizing process.

2. Propellant Toxicity Monitoring Devices (PTMD)

a. The PTMD should be portable in order to facilitate its field use by retrieval personnel. It is desirable that the PTMD be designed so that it can be carried in the retrieval pack or on the person of the retrieval personnel.

b. The PTMD should also be designed to be reliable and of the quick-response type to facilitate its use outdoors.

c. The PTMD should be capable of detection of the toxic vapors on the order of lowest concentrations of one part per million (ppm) or less. The device should also be able to detect concentrations of either propellant if possible. If the detection of either propellant by one device is impractical, then provisions for facilitating the use of the two devices should be considered.

d. The PTMD should be located in and be usable at the various locations where the propulsion subsystem may be transported, worked upon, or stored.

C. Personnel Safety Equipment

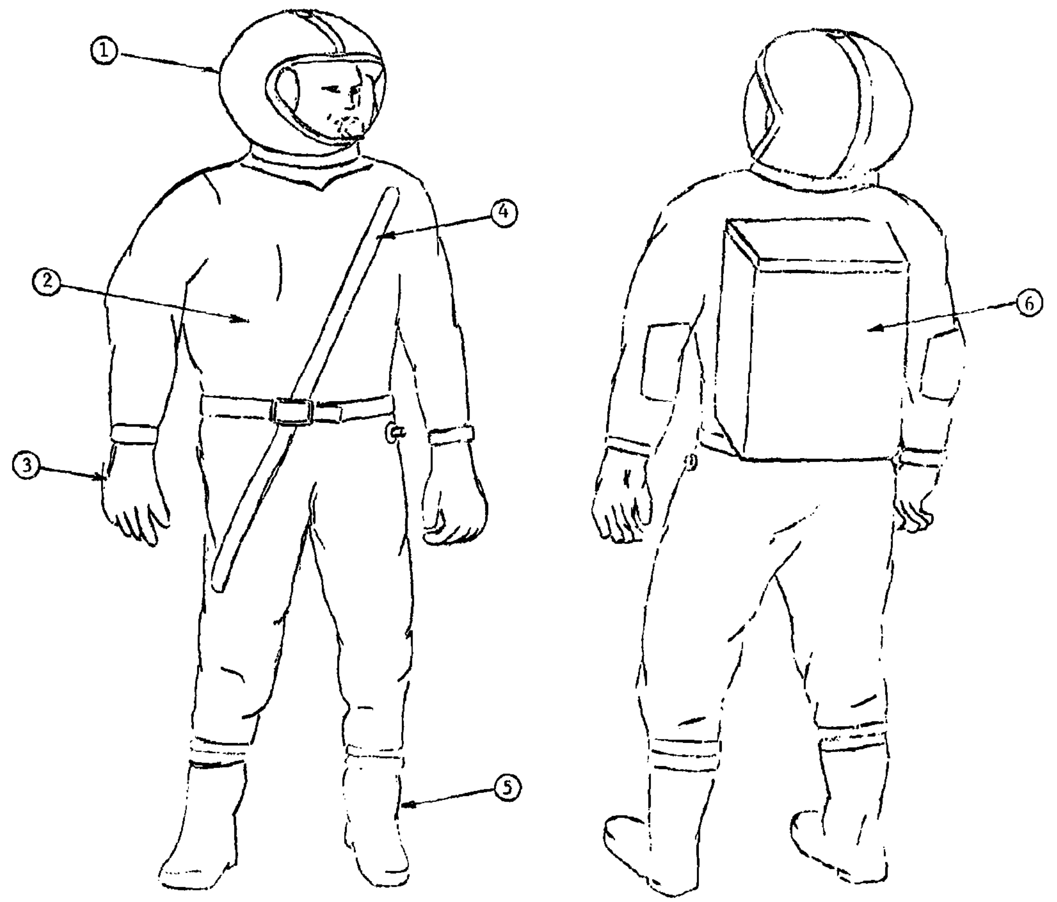
1. General

The toxicity of propellants used in advanced weapon systems has established a requirement for new concepts in the design of protective clothing and support equipment used in fuel transfer and propellant purging and neutralizing operations. For maximum wearer efficiency, it is desirable to incorporate a self-contained life support system which will satisfy the respiratory and ventilatory requirements of the wearer. The system should provide maximum mobility and comfort under expected conditions and, at the same time, protect the wearer from the toxic substances to which he will be exposed.

The system may be broken down into two major categories: (a) the protective ensemble, and (b) environmental control system.

The protective ensemble consists of all the necessary components required to create a closed envelope capable of providing complete protection from hydrazine base fuels and nitrogen tetroxide, in both the oiquid and vapor states. The ensemble must contain the internal environment (see Figures 1 and 2) created by the support system, except for the venting of excess pressure. The protective ensemble components should consist of the following: outer suit, head gear, boots, and gloves.

The environmental control system consists of those integrated components which fulfill the respiration and ventilation requirements of the person wearing the protective ensemble. There are three discrete approaches to this problem:



1	HELMET	3	GLOVE	5	BOOT
2	SUIT	4	FLAP COVERED ZIPPER	6	ENVIRONMENTAL CONTROL PACK

Figure 1. Propellant Fuel and Oxidizer Handling Suit

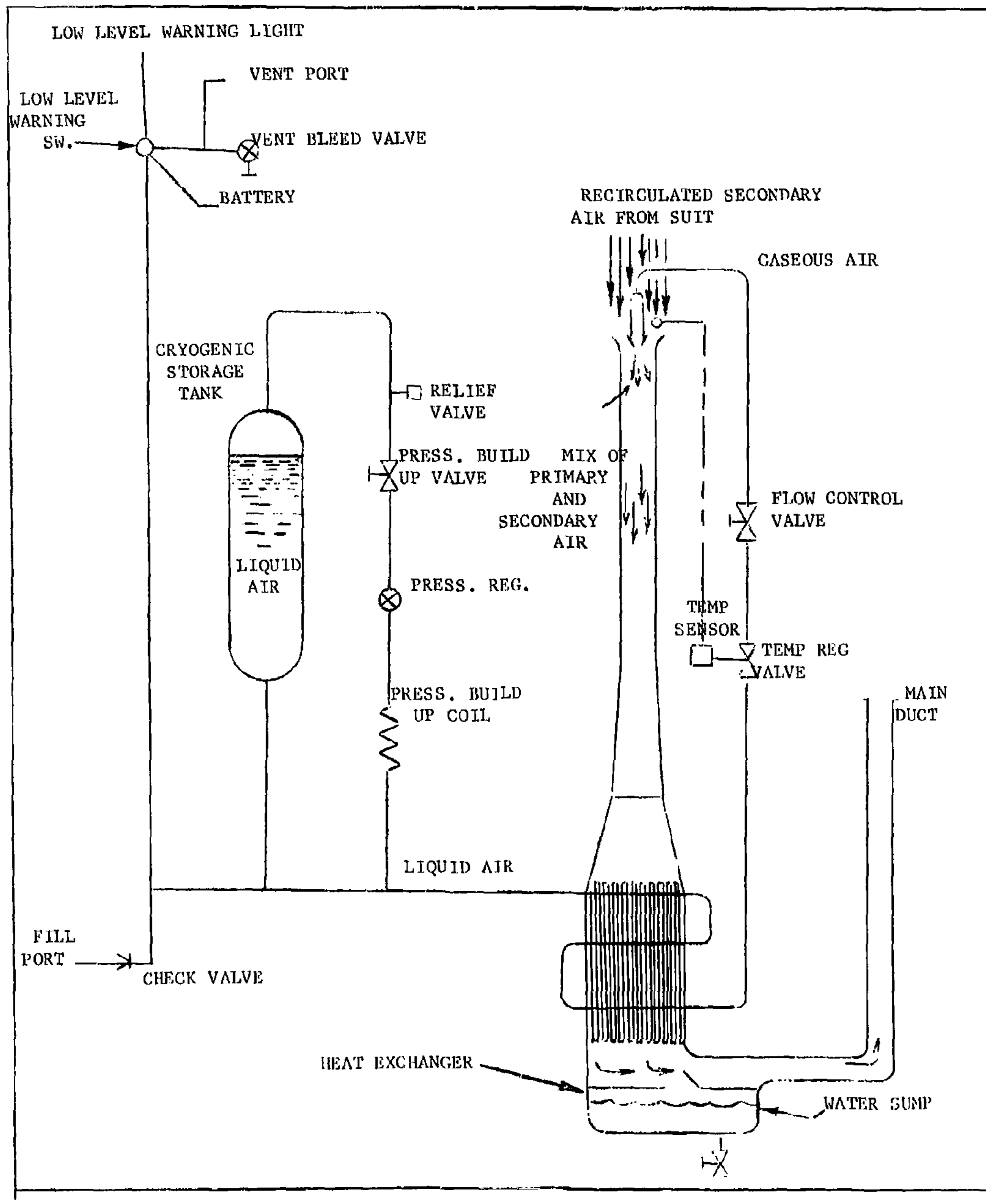


Figure 2. Schematic Diagram of Cryogenic Environmental Control System

a. Umbilical Connection

Air is forced into the suit by means of hose attached to a remote high-pressure source. A high circulation rate may be achieved in this manner, thereby assuring adequate cooling of the wearer. This system is ideal for work in a localized area, but has been all but rejected by current research teams due to the mobility restrictions imposed by the trailing air line.

b. Regenerative System

A back pack containing a compressed air supply, an air circulation system, and a means for removing CO_2 and water vapor has been tested by many research teams. Theoretically this is quite feasible, but in practice many difficulties are encountered. The logistical aspects are relatively complex; because of the many components needing recharging and/or replacement, the reliability is reduced.

c. Cryogenic System (Figure 2)

Liquid air is forced through a heat exchanger, and vaporized and ejected into the suit. Water is condensed out on the heat exchanger fins and collected in a sump. The suit remains pressurized at about one inch of water while venting overboard approximately one cubic foot of air per minute. The simplicity and functional efficiency of this approach has led to its adoption by many propellant research, manufacturing, and handling companies throughout the missile industry. It is recommended that this method be adopted for prelaunch retrieval or handling operations.

2. System Description

a. Suit

In general, the suit may be described as a gas-retaining envelope which is designed as a reasonably close-fitting garment with the helmet-hood, arms, and legs as integral parts. Boots and gloves are quick-attaching type which form a liquid- and vapor-tight seal when properly attached to the suit.

The suit could be constructed of butyl-coated fabric which weighs approximately 12 oz. per sq. yd. Total weight of the suit including boots, gloves, and helmet assembly would be approximately 10 pounds.

Preliminary research indicates that a material of this type selected for the suit offers the best resistance to propellants similar to those to be used in a program of this nature. Test programs are presently under way which are designed to determine the effect of exposure to propellants on durability, abration resistance, tear, and elongation. Additional tests are currently being conducted to determine suit life expectancies for varying ppm/time combinations.

Initially, nine sizes of suits should be provided. The basic sizes should be large, medium, and small with a long, regular, and short for each basic size. A schematic of a typical environmental control system suit is shown in Figure 2.

b. Operational Procedure

(1) Open vent port (v).

(2) Place manual pressure build-up switch and on-off control in off position.

(3) Open fill port (F) and attach fill connection.

(4) Start fill procedure.

(5) Stop fill procedure when liquid air squirts from vent port (v).

(6) Remove fill connection from fill port and cap.

(7) Cap vent port.

The system is now in a passive standby condition and may remain in this state for approximately 16 hours without excessive loss of liquid air through boil-off. When it becomes desirable to put the system in actual operational use, the following procedures apply:

(8) Place manual pressure build-up switch in the on position.

(9) Allow 1 to 2 minutes for pressure build-up.

(10) Turn on-off control regulator to on and regulate to desired air flow.

c. Operational Philosophy

Once filled, the Dewar will be exposed to a pressure build-up within the system. If the pressure exceeds 165 psi, the excess pressure will be vented through the pressure relief valve.

When the manual pressure build-up switch is turned to the on position, the external loop from the top of the tank to the bottom of the Dewar to the pressure build-up coil where it absorbs external heat and flashes into vapor. The pressure sensor allows this vapor to rise to the top of the Dewar until a pressure of 150 psi is reached. The sensor then closes the circuitry, opening intermittently to maintain this 150 psi. If the pressure exceeds 165 psi, the relief valve automatically vents off.

When the on-off variable control is turned on, the liquid air flows through the heat exchanger and into the ejector. The ejector is surrounded by a tube opening at one end to the top of the system and at the other to the heat exchanger. The force of the liquid air leaving the ejector draws ambient air into the tube and over the heat exchanger. This air is cooled by the baffle plates of the exchanger and moisture condenses out, dripping down into the water sump. The cool dry air bypasses the water sump and is directed into the air distribution system of the protective garment.

The rate of cooling is directly proportional to the rate of liquid air flow through the ejector and may be controlled by the wearer.

The duration of operation is dependent upon the rate of liquid air flow and may vary from approximately 1.25 to more than 2 hours.

To recharge the system, it is only necessary to drain water from the sump through a petcock valve and repeat charging and pressure build-up procedures.

3. Supplementary Life System Suit Considerations

It suffices to say that areas of improvement will be apparent as more and more personnel wear the initial production suits. With the advent of actual task performance, unforeseen problems no doubt will be presented.

A more detailed suit system analysis should then be provided as a subsequent report based on the initial research provided herein and include data extracted from such systems as Titan II and Advent.

a. Suit Fabric

The fabric selected for the initial production suits might be a double-coated butyl, MIL-S-4553. This has been selected (for other programs) as one of the most reliable through a series of permeability tests performed at various research facilities. Of all the materials tested, this particular one has proved by far to be one of the most resistant to permeation by both nitrogen tetroxide and hydrazine (anhydrous).

b. Environmental Considerations

In previous research tests, the wearers have been comfortable and have performed adequately in temperatures around 70°F. However, in runs of extreme cold (-30°F) and extreme heat (120°F), performance has not been entirely satisfactory. These runs have been made under conditions of high and low relative humidity. Physiological data has been recorded to determine the effects on the wearer and is presently being compiled by a Government research agency. Physiological measurements that have been made included temperature, humidity, pulse rate, heart-beat, respiratory rate, and CO_2 and O_2 concentrations. Previous suit studies of this nature have indicated certain psychological parameters that must be considered and monitored in order to assure maximum safety of the wearer.

c. Fit of Suit

Continued study and surveillance is currently being performed by various research agencies to identify problems that might arise due to physical discomfort caused by fit of suit and support pack. Further experience in performing actual tasks while wearing the suit may indicate, for example, that an extra thickness of padding is needed in the knee or elbow areas to provide the wearer with more comfort and ease of mobility over extended periods of time.

d. Donning and Removing

Standard procedures for the most efficient manner of donning and removing the suits are currently being explored. Through limited experience in the evaluation of the prototype suits, various techniques have already been employed that have decreased the time involved considerably. Some present concepts for suits currently under development have the suit zipper closing from top down, starting behind the left shoulder near the neck, running across the front of the body, and ending at the righ thigh.

This method of entry along with placing the back pack in the suit before donning has proved to be one of the most efficient methods up to this point.

e. Decontamination

The current decontamination procedure has included the use of a water shower in conjunction with a washdown with a mild caustic solution (where practicable under existing system conditions). One or more operations may be required according to the degree of contamination. The degree of contamination will be determined by a propellant toxicity monitoring device.

f. Storing

Lockers and storage containers should be designed to provide for the methods selected with adequate space for ventilation in and around suits.

g. Ventilation

The ventilation system concept presently provides air from the support pack through flexible tubes attached inside the suit to five extremities of the body. The air is released at points near each wrist, near each ankle, and at the top of the head flowing across the face. This provides an efficient system.

4. Decontamination Equipment and Kits

a. Portable sprays and water supplies should be provided as supplementary decontamination aids in the retrieval area and as such should be an integral part of the vehicles used in the retrieval operation.

b. Major facilities (e.g., vehicle receiving and storage buildings) should have provisions for personnel showers, eye baths, and wash stands.

c. Kits for retrieval personnel should contain the special antidotal solutions, lotions, ointments, emergency injections,* boric acid, etc.

d. Vehicle receiving and storage buildings should similarly be provided with the above kits.

D. Summary

The propellants used in a program of this nature require more adequate protection for personnel than that offered by many existing protective clothing systems. The system discussed consists of a vapor-tight suit and ad environmental control system for cooling, ventilation, and respiratory requirements. An on-going development program should be designed to maximize wearer comfort, system serviceability, reliability, and mobility.

* See "Influence of Large Doses of Pyridoxine Hydrochloride on the Convulsigenic Activity of UDMH In Monkeys." Report No. 62-31, School of Aerospace Medicine, USAF Aerospace Medical Center, Brooks Air Force Base, Texas. December 1961.

TABLE I. TYPICAL PROTECTIVE CLOTHING CHARACTERISTICS

FULL-PROTECTIVE GARMENT SPECIFICATIONS

Provides gas-tight protection to the wearer from toxic vapor and liquid propellants.

A. Suit

1. Butyl-coated cotton---0.015 in. thick.
2. Doubleply at back, knees, and elbows.
3. Utilizes liquid- and vapor-proof zipper.
4. Provides molded butyl liquid- and vapor-proof rings for boot and glove attachment.
5. Vents at 1/2 in. water pressure.
6. Furnished in nine sizes.

B. Helmet

1. Molded vinyl---1/8 in. thick.
2. Popout acrylic visor---1/8 in. thick.
3. Contains warning light and two-way communications system.
4.

C. Boots

1. Molded vinyl plastic.
2. Nonskid soles.
3. Furnished in eight sizes.

D. Gloves

1. Cotton-lined polyvinylchloride.
2. Furnished in four sizes.

ENVIRONMENTAL CONTROL SYSTEM SPECIFICATIONS

Satisfies physiological requirements for O_2, CO_2, temperature, and humidity.

A. General Characteristics

1. Utilizes liquid air to provide breathing air and temperature control.
2. Provides an omni-attitude performance capability.
3. Provides thermostatically controlled air flow.
4. Incorporates a visual warning system for liquid air depletion.

B. Specific Performance Characteristics

1. Operates normally between 120°F and -20°F.
2. Dewar capacity.................... 3.3 liters.
3. Flow rate.......................... 10 cfm.
4. Operating pressure................. 150 psi.
5. Heat exchange rate ....1100 Btu/hr max.
6. Relative humidity provided in suit... 65% max.
7. Operating time....1 hr. min., 1-1/2 hrs.max.
8. CO_2 concentration under exercise conditions ....1%/hr.
   No exercise .... 0.5%/hr.
9. Standby time.............. 30 hrs. max. rec.
10. Total weight (including harness)..... 21 pounds

V. HANDLING OF HYPERGOLIC PROPELLANTS

A. General

Because of the hazardous nature of the propellant subsystem, certain specific handling techniques should be followed in working with or handling nitrogen tetroxide and hydrazine (anhydrous) propellants.

B. Handling Methods and Techniques

1. Hydrazine (Anhydrous):-The following comments are a compilation of known and proven handling methods and procedures currently being practiced in the propellant industry.

a. Equipment and material to be used in hydrazine storage and/or transfer should be coordinated through a specifically designated safety officer to insure compatibility of materials during handling activities. This would include gasketing, sealants, and lubricants.

b. Containers used for storage of hydrazine and/or hydrazine and other chemicals should be shielded or shaded from the direct rays of the sun in the heat of the day, particularly during transfer and purging activities.

c. Equipment used for the handling of hydrazine should be cleaned, pickled, and otherwise prepared for use according to approved procedures.

d. If at all possible, hydrazine handling should be isolated from oxidizing materials and vapors, combustible materials, and inflammable areas.

e. Containers used for storage of hydrazine after hydrazine handling should be kept tightly sealed.

f. Every precaution should be taken to prevent manifolding of hydrazine with the oxidizer during handling.

g. Prior to handling of hydrazine, a very thorough inspection (if possible) should be made to determine if there has been any leakage.

h. Drums, tanks, transfer and purging equipment should be thoroughly flushed with water and dried after each use.

i. Approximately 10% ullage should be provided for in filling tanks with or transferring hydrazine. A nitrogen atmosphere should be maintained in the space above the liquid.

j. Care should be taken to avoid spillage; if a spill does occur, or if a leak is discovered, the hydrazine should be thoroughly flushed to drain away any excess quantities.

2. Nitrogen Tetroxide: -The following comments are a compilation of known and proven handling methods and procedures currently being practiced in the propellant industry.

a. N_2O_4 should be handled in areas isolated from combustibles, particularly during transfer and purging activities.

b. In the event of container valve leakage, the container (tank, etc.) should be positioned to discharge gas instead of liquid until contents can be cooled and the container decontaminated.

c. During handling and purging activities, containers <u>will not</u> be heated to discharge gas or liquid under any conditions.

d. Personnel shall remove protective valve covers and outlet caps with caution, standing to one side as protection against leaky valves or pressure build-ups.

e. Transfer lines should contain a valved vent terminating in a safe direction to relieve pressure in the transfer before purging and/or transferring and also prior to disconnecting the transfer line coupling.

f. All handling should be in open areas which afford natural ventilation.

g. Tanks containing N_2O_4 should be shielded to protect them from the heat of direct sunlight during the heat of the day.

C. <u>Precautionary Measures</u>

1. Hydrazine (Anhydrous):-The following comments are included as steps or measures to be taken to insure "complete safety" of personnel and equipment while working with or observing hydrazine activities. Each operator assigned to work with hydrazine should be thoroughly familiar with and trained in the use of specific operating procedures and instructions while working with hydrazine during handling operations.

a. No operator should work alone on equipment in use with hydrazine.

b. All equipment must be carefully checked and made ready before the operation starts to afford the protection intended. Clothing should be clean and, if possible, nonflammable.

c. Where available, safety showers should be tested prior to the start of operations and charged hoses made ready for immediate use.

d. Food must not be stored or eaten in areas where hydrazine is handled.

e. Operators should thoroughly wash their hands after working with hydrazine and hydrazine equipment.

f. Respiratory protection must not be overlooked in any rescue in a hydrazine-contaminated atmosphere.

g. Leaks should be corrected at once.

h. The continuity of all ground wires should be checked to prevent a faulty ground which could result in a spark and hence explosion or fire.

i. Hydrazine transfer equipment should be maintained in excellent condition. Any leaks should be corrected (if at all possible) at once.

j. Work permits, other than in the retrieval area, should be required for all work by personnel concerned with hydrazine.

2. Nitrogen Tetroxide: -The following comments are included as steps or measures to be taken to insure "complete safety" of personnel and equipment while working with or observing nitrogen tetroxide activities. All personnel assigned to work in N_2O_4 storage and handling areas should be thoroughly familiar with and trained in the use of specific operating procedures and instructions while working with N_2O_4 during handling activities.

a. No operator should work alone on equipment in use with N_2O_4.

b. All handling and transfer equipment should be checked out to preclude any leakage to atmosphere.

c. All safety equipment should be carefully checked and made ready prior to the operation, to afford the protection intended. Clothing should be clean and if possible nonflammable.

d. Safety showers, where available, should be tested prior to the start of the operation and charged hoses made ready for immediate use.

e. Food must not be stored or eaten in areas where N_2O_4 is handled.

f. Operators should thoroughly wash their hands after working with N_2O_4 and N_2O_4 equipment.

g. Respiratory protection should not be overlooked in any rescue in an N_2O_4 contaminated atmosphere.

h. Leaks should be corrected at once if possible.

i. Work permits, other than in the retrieval areas, should be required of all personnel concerned with N_2O_4 activities.

D. Emergency Measures

1. Emergency measures, equipment, and procedures should be provided for operations involving the use of hydrazine (anhydrous) and nitrogen tetroxide. Such measures, equipment, and procedures should include, but not be limited to, the following:

a. When work is of an emergency nature or if an activity requires that an operator be physically located in an area or precarious position with regard to escape, one operator must position himself at a distance to observe the operation, acting as a "buddy" to call for help or effect a rescue.

b. Nitrogen tetroxide can be neutralized to an effective degree in an emergency situation by water (reacts in presence of oxygen to form nitric acid-toxic), hydroxy acetic acid and/or triethanolamine. Water, obviously, is generally more often available.

c. Hydrazine (anhydrous) can be also neutralized by water, alcohol (higher value), and liquid ammonia.

d. Emergency respirator equipment should always be present (if possible); all personnel should be trained and proficient in its use.

e. Emergency suits, self-contained oxygen breathing equipment, masks and containers, and gloves should be provided; all personnel should be trained and proficient in their use.

f. Emergency decontamination equipment, such as water tanks (open-dunking type), shower baths (eye and personnel type), and charged water hoses, should be provided; all personnel should be trained and proficient in their use.

g. Emergency instructions/procedures should be provided for anticipatory emergency situations; all personnel should be trained and proficient in their use.

h. Emergency conditions resulting from fire or explosion should be treated with the same caution and care as in other emergency conditions; however, personnel must be evacuated and a trained propellant fire and explosion team should be called. If this situation occurs in the retrieval area, personnel should evacuate the area immediately, unless the situation is obvious and instructions are provided to the retrieval team designating otherwise.

VI. HYPERGOLIC PROPELLANT TRAINING

A. Introduction and Discussion

It is recognized that due to the nature of the propellants involved (hypergolic, toxic and flammable), considerable attention must be given to the training of military and civilian retrieval personnel in order to assure maximum safety of personnel and equipment.

A detailed training plan should be developed based on research for this document, and should encompass the following areas:

1. Preliminary training plan details.
2. Training equipment and simulators.
3. Training manuals, aids, and devices.
4. Training propellant handling facilities.

Additional data on hypergolic propellants and handling methods is currently being gathered and should serve as supplementary information for inclusion in the forthcoming training documents to be published by the authors.

VII. CONCLUSIONS

A. Summary

Consideration has been given to the problems and hazards, handling methods and techniques, equipment required for handling and monitoring, safety considerations both for personnel and equipment, training and training equipment for hypergolic propellants — specifically, nitrogen tetroxide (oxidizer) and hydrazine (fuel).

B. Recommendations

In summary, then, it appears that continuing design review, testing, and field evaluation will be required in order to assure that a safe, reliable, and operable hypergolic propellant handling subsystem be provided for integration with the total retrieval operations system.

APPENDIX 1. SPECIFIC WEIGHTS FOR MOST COMMONLY USED STORABLE PROPELLANTS

Oxidizers	Lb per Gal.
Nitrogen tetroxide, N_2O_4	12.1
Fuming nitric acid	
Type IA	12.6
Type IIIA	13.0
Hydrogen peroxide (98%), H_2O_2	12.0
Chlorine trifluoride, CF_3	15.2
Perchloryl fluoride, CO_3F	11.9
Fuels	
Unsymmetrical dimethylhydrazine, UDMH	6.5
Hydrazine, N_2H_4	8.4
Furfuryl alcohol	9.4
Aniline	8.5
RP-1 - Fuel	6.7
JP-4 - Fuel	6.5
JP-X (60% JP-4/40% UDMH)	6.5
ANFA (30% aniline/70% furfuryl alcohol)	9.2
Aerozine - 50	7.5
Monomethyl hydrazine, MMH	7.3
Pentaborane, $B_5 H_9$	5.1

At 70°F and 14.696 psia conversion factors, 1 cu. ft. =7.481 gals.

APPENDIX 2. TYPICAL PROPELLANT CHARACTERISTICS

Theoretical thrust chamber.

Propellant	Application	Specific impulse at 500 psi		Bulk Density (lb/ft^3)	Optimum Mixture Ratio	Combustion Temperature (°F)
		Sea Level (sec)	In Space (sec)			
Liquid oxygen and hydrocarbon fuel (kerosene)	Booster & sustainer	261	324	63	2.25	5,800
$F_2 - NH_3$	Booster & sustainer	301	368	71	2.77	7,200
$F_2 - H$	Booster & sustainer	364	447	18	4.00	4,700
$F_2 - N_2H_4$	Booster & sustainer	303	372	80	1.75	7,300
$O_2 - H_2$	Booster & sustainer	357	441	16	3.50	
Acid UDMH	Booster & sustainer	246	304	62	2.40	5,100
Monopropellant 90% $H_2 - O_2$	Vernier	137	169	87	---	1,365
$N_2H_4 - N_2O_4$	Booster & sustainer	260	320	85	1.93	6,000

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